Technical Summary Report

for

Low-Cost Production of Nano-Pyrotechnics

Ordnance Technology Initiative Team
Dennis Wilson
John Granier
Aaron Taylor

Initiative Team Technical POC
Dr. Dennis Wilson
Energetic Materials and Products, Inc.
Round Rock, TX 78681

REPORT DOCUMENTATION PAGE	*Form Approved* **OMB No. 0704-0188**

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
30-07-2010	FINAL TECHNICAL REPORT	25-07-2009 - 25-07-2010

4. TITLE AND SUBTITLE LOW-COST PRODUCTION OF NANO-PYROTECHNICS	**5a. CONTRACT NUMBER** W15QKN-09-9-1001
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) DR. DENNIS WILSON DR. JOHN GRANIER AARON TAYLOR	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ENERGETIC MATERIALS AND PRODUCTS, INC 1413 BRANDI LANE ROUND ROCK, TX 78681	**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) ADVANCED TECHNOLOGY INTERNATIONAL 5300 INTERNATIONAL BLVD. CHARLESTON, SC 29418	**10. SPONSOR/MONITOR'S ACRONYM(S)** ATI
	11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
It was the objective of this study to find a low-cost, environmentally friendly percussion primer composition replacement for use in the standard M42 primer widely used by the military for center-fire ammunition. A BAM fallhammer apparatus, ball-drop primer testing apparatus, and an ESD sensitivity testing device were all designed, fabricated, and implemented for material screening. Thermites, as a class of reactive material, are suited to this application because they produce no harmful by-products, and the pre-cursor materials are relatively inexpensive. Nano-thermites have been previously studied; however they are expensive and are not suitable as low-cost replacement. In an attempt to reproduce nano-thermite sensitivities, inexpensive 2µm aluminum flake was ball-milled and coated with a reactive PFPE layer in an attempt to reduce particle size, increase specific surface area, and create a more impact sensitive mixture. Various oxidizers and other additives were also explored. During the course of the one year study, over 50 different compositions were fabricated and tested, yet no suitable low-cost replacement was found within the desired sensitivity levels.

15. SUBJECT TERMS
Percussion Primer, Impact Sensitivity, Thermite, Nano-thermite, aluminum, metal oxide, ball milling, green energetic

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	SAR	25	AARON TAYLOR
U	U	U			**19b. TELEPONE NUMBER (*Include area code*)** 512-380-1992

on Technical/Cost/Schedule Performance:

EMPI successfully obtained a wide variety of materials suitable for low-cost, green primer composition fabrication including fuels, metal oxidizers, abrasives, and binders. EMPI also successfully designed, fabricated, and developed a wide array of reactive material fabrication and test equipment in order to screen many different primer compositions. These include a ball drop primer tester and pressure bomb, BAM impact sensitivity tester, electro-static discharge sensitivity tester, ball mill and grinding media, and a multi-primer loading tool. All of this equipment is fully functional and was used in screening dozens of potential primer compositions.

The compositions in the Group A formulation matrix were fabricated, loaded into primers, and tested for impact sensitivity with the ball drop primer tester. None of the primers successfully fired with maximum impact, so progression to a Group B set of compositions was postponed. A baseline MIC (nano- thermite), with known success in percussive primer applications, was fabricated in order to refine EMPI's fabrication and primer loading procedures for increased impact sensitivity. The refining process resulted in an increase in impact sensitivity for the baseline MIC on the ball drop tester from 10% of primers firing at the maximum height of 20 inches to consistent impact sensitivities of 11 to 12 inches. As a result of this success, as well as acquiring some results from material characterization testing, this project progressed forward with a Group B set of formulations.

The Group B formulation matrix was devised. EMPI exhausted the majority of the obtained primer cup assemblies in the Group A matrix screening and the baseline MIC screening. No source for additional primer cup assemblies was found. As a result, the initial Group B testing (Group B alpha) was to be screened by determining the impact sensitivities of the formulations in loose powder form via the BAM Impact Tester apparatus

No successful ignitions occurred for any primer composition materials in the BAM impact tester even when the sensitivity range was increased from 5 J to 25 J by designing and fabricating additional drop masses. Actions taken to address this problem included sending the material to an outside source to be tested for sensitivity and using materials with known impact sensitivities in EMPI's BAM tester for calibration purposes. Calibration consisted of rebuilding the concrete base to ensure maximum stability, and a 1 inch layer of smooth concrete was poured on top of the base and carefully leveled. Once the concrete layer was set and level, the impact tester was re-assembled using carefully placed steel shim stock to ensure that each component was properly aligned. Once calibration was completed, a Bruceton analysis found an acceptable impact sensitivity of 6.1 J for PETN.

It was determined that loose powder impact sensitivities have no direct correlation with loaded percussion primer cup sensitivities. As a result, the remaining primer cups (80) were divided into four groups to form and abbreviated Group B matrix in order to continue testing. All four compositions used the 2 μm aluminum flake in an effort to find a composition that met the "low-cost" aspect of the program. Unfortunately, no successful primer fires occurred for these four compositions.

Information:

Technical Achievements:

The following is an account of the progress that occurred during the course of the one year Nano-Pyro program from 14 July 2009 to 14 July 2010, or since the last submitted quarterly technical report.

Materials

Materials in each of three reactants classifications, fuels, reactants, and abrasives, were acquired.

Aluminum flake was obtained from the pyrotechnics company Firefox in two varieties: Indian Black and German Black. In order to determine which flake was more suitable to the goals of this project, samples of each were sent to ARDEC for chemical analysis (SEM, etc.). The two primary fuel sources tested were the aluminum flake as manufactured and the aluminum flake after applying a ball mill coating of perfluorinated polyether (PFPE).

Table 1 Fuel Reactants Specifications

Material	Vendor	Part #	Price	Description
2μm Al flake	Firefox	C103GBB-FS	\$0.04/g	German black, flash blend
2μm Al flake	Firefox	C104-FS	\$0.04/g	India black, ground flake

Metal oxide nano-powders of various sizes and chemical compositions were used as the oxidizer reactants. We acquired two types of Fe_2O_3, CuO, two types of Bi_2O_3, and two types of MoO_3.

Table 2 Metal Oxide Reactants Specifications

Material	Vendor	Part #	Price	Description
20-40 nm Fe_2O_3 powder	Alfa Aesar	45007	\$0.59/g	Surface area: 30-60 m^2/g
3 nm Fe_2O_3 powder	Alfa Aesar	44119	\$1.32/g	Surface area: 250 m^2/g
30-50nm CuO powder	Alfa Aesar	44663	\$1.77/g	Surface area: 13 m^2/g
<1 μm Bi_2O_3 powder	Clark Manufacturing	N/A	.04/g	Median particle size: 800nm
70 μm agglomerate	Clark Manufacturing	N/A	.05/g	Agglomerate of the <1 μm powder
Densified MoO_3 powder	Climax Molybdenum	SP198K		
Un-densified MoO_3 powder	Climax Molybdenum	UO13K		

Abrasives can be added to the primer composition in order to increase the impact sensitivity of the material. Two types of materials were acquired to serve this purpose: SiC and Sb_2S_3. We have acquired SiC in both 1μm and 40μm distributions from Washington Mills. Antimony sulfide was the leading possibility because it also acts as a fuel. A 200 mesh Sb_2S_3 powder has been obtained from Sigma Aldrich.

Table 3 Abrasive Reactants Specifications

Material	Vendor	Part #	Price	Description
1μm SiC powder	Washington Mills	FP-12	$0.01/g	Median grit size: 1.25 μm
360 mesh SiC powder	Washington Mills	F360 RA	$0.005/g	Maximum grit size: 44 μm
200 mesh Sb_2S_3 powder	Sigma Aldrich	244562	$0.20/g	Maximum grit size: 74 μm

Test and Material Preparation Equipment

The following is a discussion of the equipment for the manufacturing and testing of the primer compositions.

Ball-Drop Tester

A ball drop primer tester and accompanying pressure bomb were designed and fabricated in order to test the sensitivity of fully loaded and assembled primer configurations. The ball-drop tester and pressure bomb was used successfully in testing factory made M42 primers as well as both the baseline MIC primers and the novel, low-cost "green" primer compositions. The entire ball drop tester apparatus and the specialized pressure bomb are shown in Figure 1 and Figure 2, respectively. The ball drop tester can accommodate either a 2 or 4 oz. ball dropped from a maximum height of 20 inches, allowing for a wide range of impact forces. Two firing pins were also fabricated, 0.050" and 0.090", for use with different primer configurations. The pressure bomb is equipped with a photodiode and pressure transducer in order to determine the differences in the speed of the pressure wave and the reaction itself. These apparatus have been tested successfully using factory made primers. The M42 primers fired in the appropriate sensitivity range.

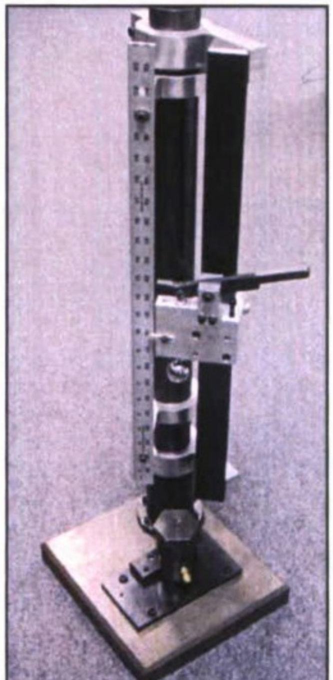


Figure 1 Ball drop primer tester

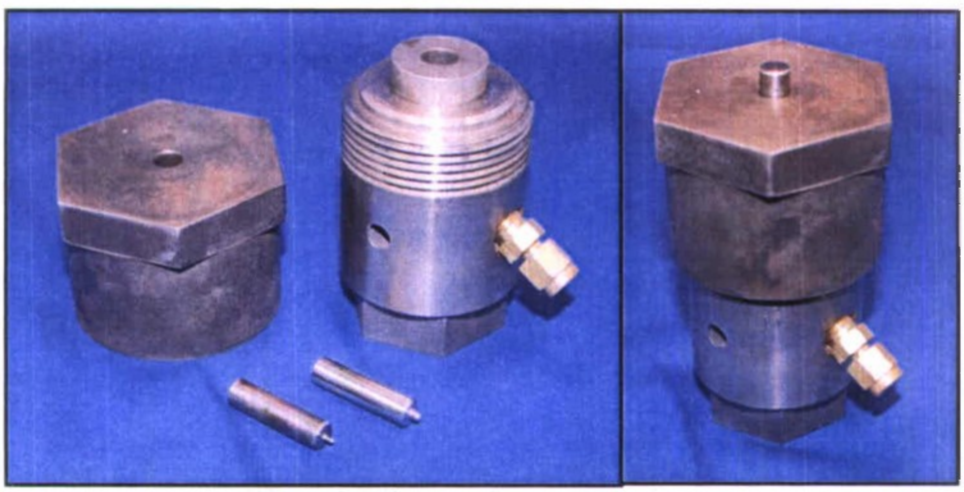


Figure 2 Primer testing pressure bomb

Figure 3 shows a sample trace of the reaction and pressure waves acquired in the pressure bomb for a factory lead styphnate primer and a baseline MIC primer. The pressure wave peaks at 470 psi approximately 75 micro-seconds after the reaction occurs for the M42 primer and at 130 psi approximately 110 micro-seconds after the reaction for the MIC primer.

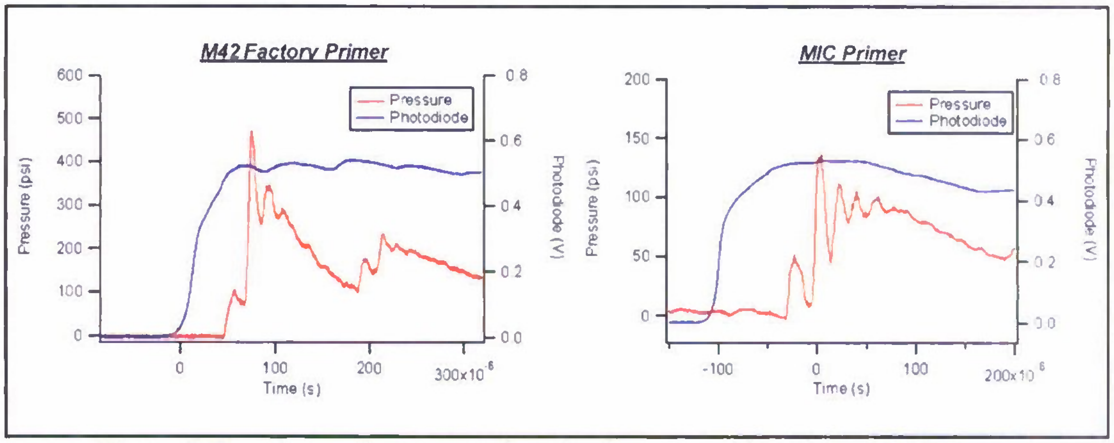


Figure 3 Reaction and pressure plots for factory and baseline MIC primers

Ball Mill

A used U. S. Stoneware 755RMV ball mill was acquired, and is shown in Figure 4. U.S. Stoneware jars (size 000) with 0.3L capacity were used for the milling, along with an assortment of grinding media. The three types of grinding media were 0.5"x0.5" Berundum cylinders, 0.25"x0.25" Berundum cylinders, and higher density 0.5"x0.5" zirconia cylinders, and are shown in Figure 4 along with a 000 jar.

The ball mill was used in the milling of 2 micron aluminum flake. Multiple batches were processed with varying time lengths (0 – 48 hours), solvents, and concentrations of PFPE (0% - 10%).


Figure 4 Ball mill with ¼ H.P., 20-300 rpm, 115/110V motor.

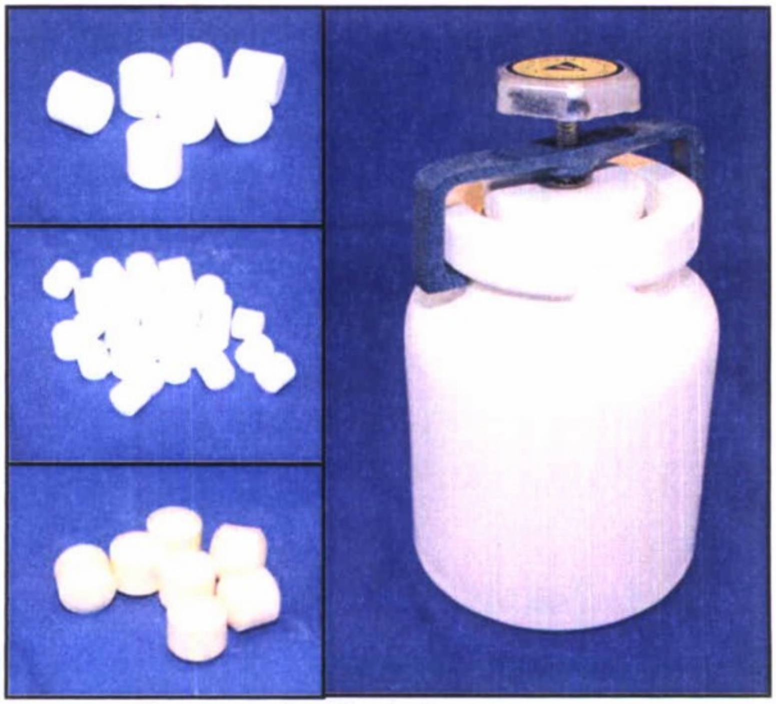


Figure 5 Ball mill grinding jar and media

Primer Load Tool

The tool acquired from ARDEC, shown in Figure 6

Figure 6 was originally used to load and press single primer cups, which was adequate for the initial testing phases. There were several problems with this primer loading tool and the procedures used, which will be discussed further.

Figure 6 Single primer loading tool

A primer loading tool was designed and fabrieated in order to aecommodate loading multiple primers simultaneously as well as new, refined primer loading procedures. In eonjunction with the new primer loading tool, a die puneh fitted for use in an arbor press has been designed and fabrieated. As shown in Figure 7**Error! Reference source not found.**, the primer loading tool holds 25 primer eups for simultaneous loading, and the die punch, used for consolidating the loaded primer composition, is shaped convexly in order to allow a better mate between the anvil and powder surfaees. The refined loading procedures will be diseussed further.

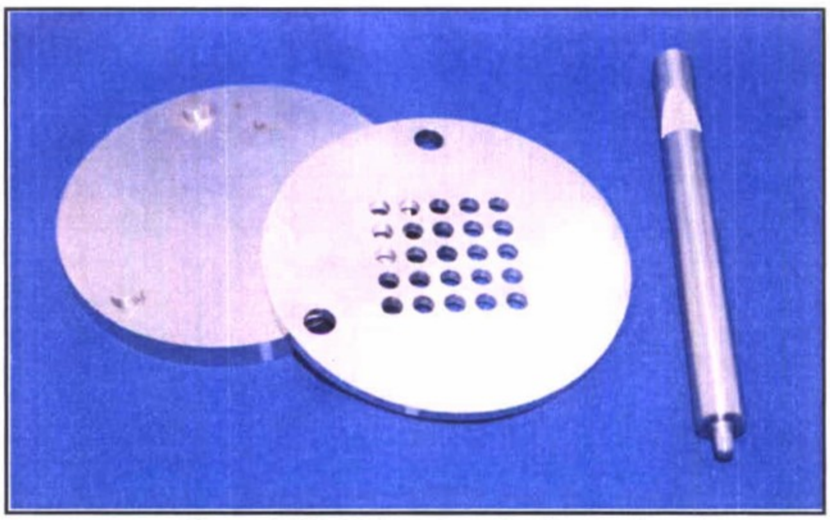


Figure 7 Multiple primer loading tool

BAM Impact Tester

A fall-hammer BAM impaet tester was designed and fabrieated by EMPI for testing the impact sensitivity of the various primer compositions in loose powder form. The BAM impaet tester is a eommonly accepted deviee for impaet sensitivity testing. Figure 8 shows the tester with close-ups of the impact earriage and anvil assembly. As originally designed, the tester was able to test sensitivities up 5 Joules with a drop weight of 1 kg, maximum drop height of 22 inches. 30 mm^3 of bulk powder is loaded between two flat, polished circular surfaces with 10 mm diameters.

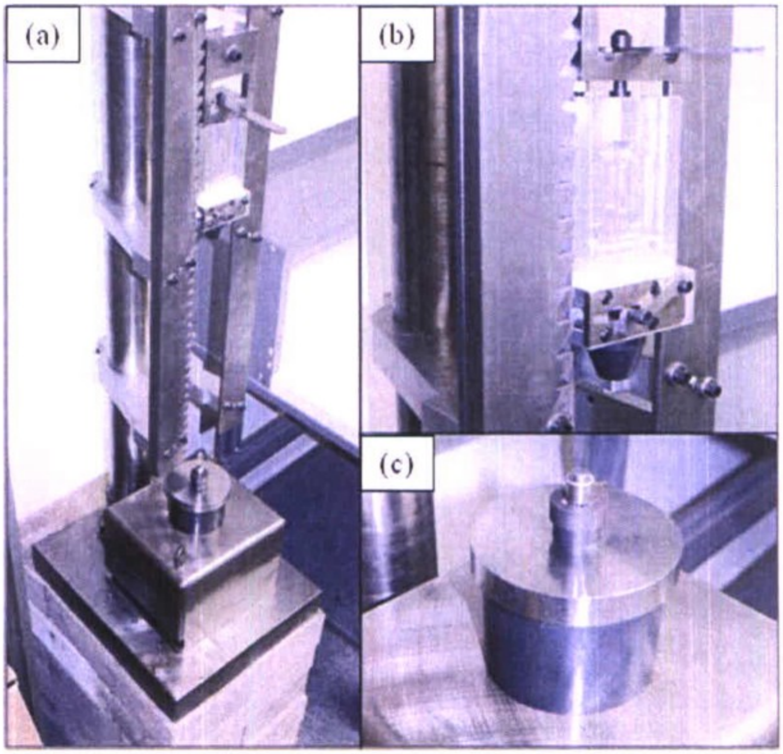


Figure 8 (a) Impact sensitivity tester, (b) impact carriage, and (c) impact anvil

ESD Tester

Components of an existing electro-static discharge tester were acquired and reconfigured to meet the requirements of this project. An ESD tester is used to test the sensitivity of loose powders to electro-static discharge by passing a high-voltage spark through the sample. Figure 9Figure 9 shows the basic electrical schematic on which the ESD tester operates. A 25kV power source was used for the re-worked design.

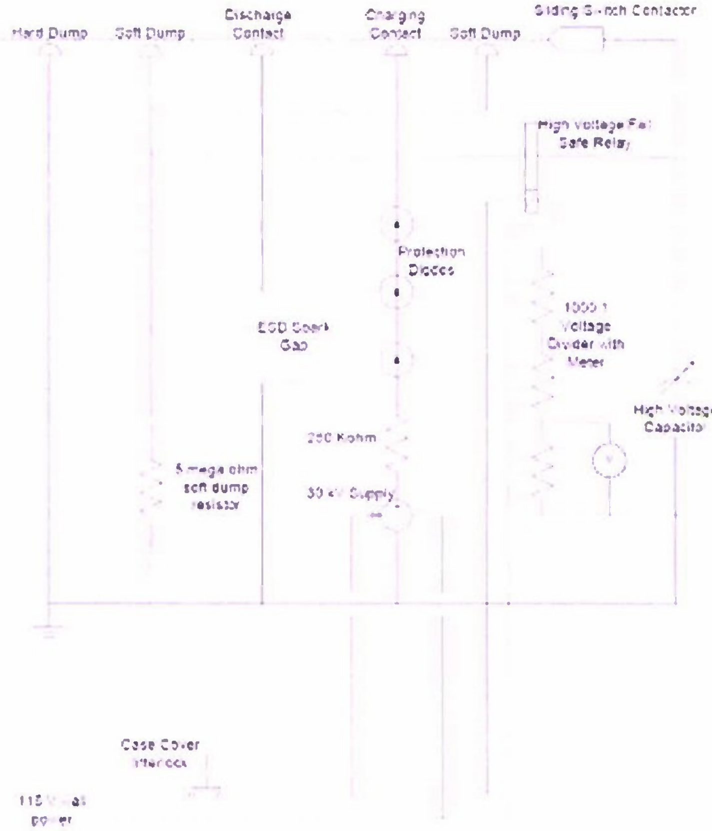


Figure 9 ESD tester electrical schematic

Figure 10 shows the assembled ESD tester. The powder sample is loaded into the sample cup, which along with the electrodes, is housed in a protective Lexan box. Two different capacitors were acquired in order to accommodate a wider range of sensitivity testing. A 0.218 μf capacitor allows sensitivity testing in the range of 150 mJ – 68 J, and a 0.0297 μf capacitor provides 15 mJ – 9.3 J.

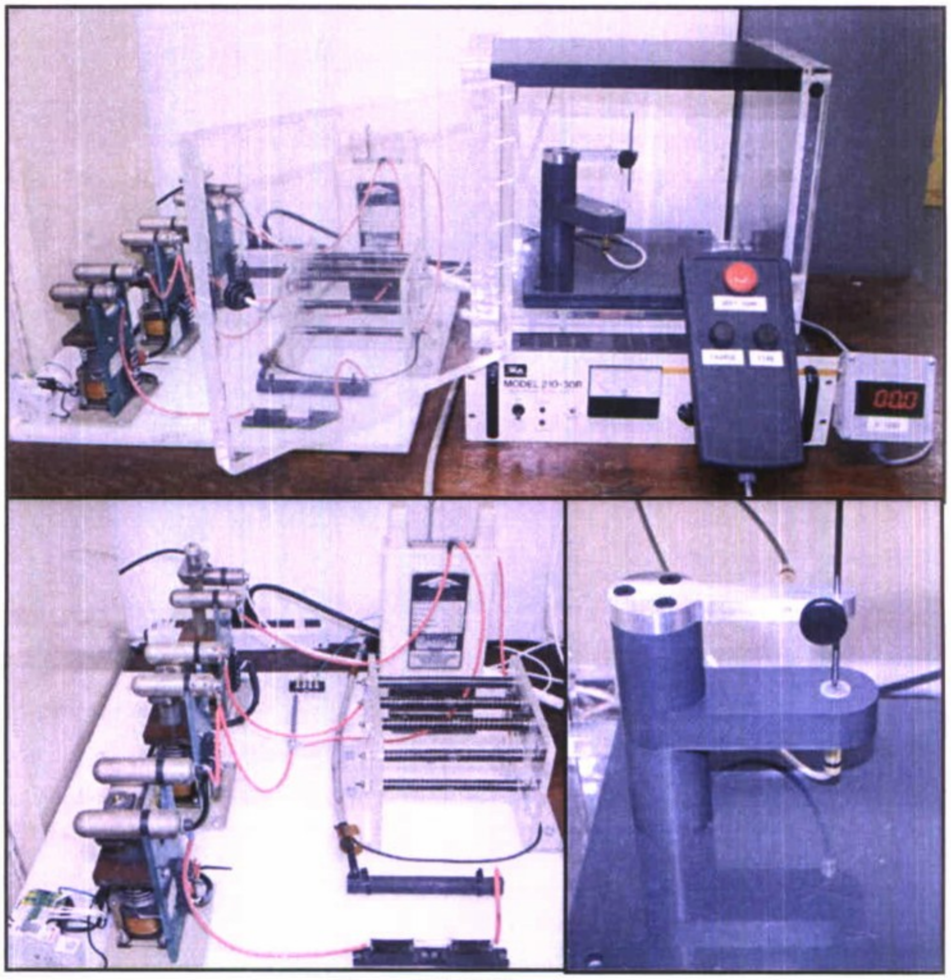


Figure 10 ESD tester

Initial Primer Composition fabrication and planning (Group A)

The following is a discussion of the formulation and design of the first group of primer composition testing. Table 4 illustrates the original test matrix for Group A. For the ball mill coated aluminum, α and β represent PFPE concentrations of 1% and 3%, respectively. The _p and _s indicate whether pure PFPE or PFPE plus solvent will be used in the coating procedure.

Table 4 Group A Test Matrix

Legend	
Ab	Abrasive
SW2, 6	Sonic wand, time min.
SB10, 30	Sonic bath, time min.
BM1	Ball mill, time hr

Group A

Code #	Fuel	Oxidizer	Other	Process
4114A01	2um Al flake	MoO_3 (dense)	Ab, Binder	SW2, DMF
4114A02	2um Al flake	MoO_3 (undense)	Ab, Binder	SW2, DMF
4114A03	2um Al flake	MoO_3 (dense)	Ab, Binder	SW2, DMF
4114A04	2um Al flake	Bi_2O_3 (<1 μm)	Ab, Binder	SW2, hexanes
4114A05	2um Al flake	Bi_2O_3 (<1 μm)	Ab, Binder	SW2, hexanes
4114A06	2um Al flake	Bi_2O_3 (<1 μm)	Ab, Binder	SW2, hexanes
4114A07	Al, PFPE α_p	MoO_3 (dense)	Ab, Binder	BM6 PFPE (1%) SW2, DMF
4114A08	Al, PFPE α_s	MoO_3 (dense)	Ab, Binder	BM6 PFPE (1%) + solvent PFS2 SW2, DMF
4114A09	Al, PFPE β_p	MoO_3 (dense)	Ab, Binder	BM12 PFPE (3%) SW2, DMF
4114A10	Al, PFPE β_s	MoO_3 (dense)	Ab, Binder	BM12 PFPE (3%) + solvent PFS2 SW2, DMF
4114A11	Al, PFPE α_p	Bi_2O_3 (70 μm agg.)	Ab, Binder	BM6 PFPE (1%) SW2, hexanes
4114A12	Al, PFPE α_s	Bi_2O_3 (70 μm agg.)	Ab, Binder	BM6 PFPE (1%) + solvent PFS2 SW2, hexanes
4114A13	Al, PFPE β_p	Bi_2O_3 (70 μm agg.)	Ab, Binder	BM12 PFPE (3%) SW2, hexanes
4114A14	Al, PFPE β_s	Bi_2O_3 (70 μm agg.)	Ab, Binder	BM12 PFPE (3%) + solvent PFS2 SW2, hexanes

The goals of Group A testing were to study primer formulation function and to evaluate the following:

1. Ball mill coated aluminum
2. Mixing procedure (ball milling times, sonic bath/wand times, solvents, etc.)
3. Optimum abrasive material and concentration

4. Initial study of metal oxide nano-powders

Three versions of formulation 4114A01 (Figure 11a-c) with varying abrasive concentrations were created and tested in order to determine an initial baseline for the primer composition. Abrasive concentrations of 10%, 15%, and 20% were chosen for testing based upon existing primer formulations.

After mixing and testing the initial primer compositions, a determination was to be made as to whether or not a binder material is necessary. Binder materials in consideration were common binding materials such as gum arabic or Viton. An iterative process similar to that used to determine abrasive concentration was incorporated with binder concentrations of 0.5%, 1.0%, and 1.5%. The images shown in Figure 11 were taken using an optical microscope to depict the homogeneity and concentration of the white abrasive particles. The images are not good quality due to depth of field and illumination difficulties.

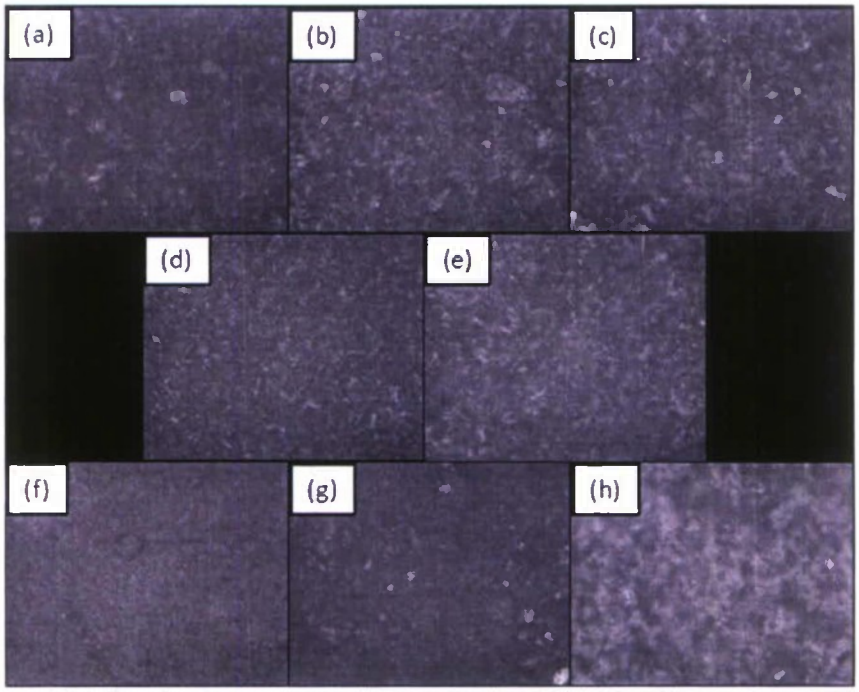


Figure 11 Mixed primer compositions: (a-c) 4114A01 with varying abrasive concentrations, (d) 4114A02, (e) 4114A03, (f) 4114A04, (g) 4114A05, and (h) 4114A06

Group A Formulation Screening

The original Group A formulation matrix (Table 4) submitted in to ARDEC was modified and expanded. It was originally intended to use the information gained from compositions 4114A01-4114A06 to determine which fuel (German or Indian flake aluminum) and oxidizer morphologies would be used in the subsequent compositions. However, since no compositions led to successful fires in the ball drop apparatus and little to no information was gained, the Group A matrix was expanded in order to provide a more thorough screening. Also, it was determined that due to both proper ball-milling procedures and safety reasons, all aluminum milling would occur in the presence of a solvent. As a result, PFPE concentrations of 5% and 10% were added to the 1% and 3% already in the matrix. The expanded Group A matrix is shown in Table 5.

Five to ten primers were loaded of each composition in Group A and tested with the ball drop tester. There were no successful fire events for any of the compositions. In response to the lack of success, several steps were taken in order to order to expose potential problems before proceeding with a Group B screening. Samples of ball-milled aluminum were sent out for BET testing in order to determine the ball milling effect on the specific surface area (SSA) of the aluminum particles. Theoretically, SSA is an important factor for the sensitivity of the reactive materials; the more surface to surface contact between the fuel and oxidizer particles, the more reactive the material. Four samples were tested: 2 micron aluminum flake after ball milling for 48 hours, 24 hours, 12 hours, and no ball milling. The results of the four BET tests are included in Appendix A. The SSA of the 80 nm aluminum spheres used in traditional MIC is 26.1 m^2/gm, and it was hoped that ball milling aluminum flake could provide comparable numbers. The SSA of the four samples was 12.0, 13.1, 11.4, and 6.9 m^2/gm for ball milling times of 0, 12, 24, and 48 hours, respectively. These results are shown in Appendix A. The proposed explanation for this downward trend in SSA is that the repeated impacts of the grinding media rounds and smoothes the malleable aluminum flake, thereby reducing SSA. Since the SSA of the 0 hour and 12 hour milled aluminum flake is much higher than anticipated, one proposed solution to this problem is to ball mill the harder, more brittle metal oxide particles. This may increase the SSA of the oxidizer particles, resulting in more surface to surface contact between the fuel and oxidizer particles.

Another step taken to determine potential problems with Group A testing was to fabricate and characterize a baseline MIC (nano-thermites), which have shown adequate sensitivity and performance in percussive primer applications by other organizations.

Table 5 Group A (Expanded) Test Matrix

Legend	
Ab	Abrasive
SW2, 6	Sonic wand, time min.
SB10, 30	Sonic bath, time min.
BM1	Ball mill, time hr

Group A (Expanded)

Code #	Fuel	Oxidizer	Other	Process
4114A01	2μm In Black	MoO_3 (dense)	Ab (Sb_2S_3)	SW3, DMF
4114A02	2μm In Black	MoO_3 (undense)	Ab (Sb_2S_3)	SW3, DMF
4114A03	2μm Ge Black	MoO_3 (dense)	Ab (Sb_2S_3)	SW3, DMF
4114A04	2μm In Black	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	SW3, hexanes
4114A05	2μm In Black	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	SW3, hexanes
4114A06	2μm Ge Black	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	SW3, hexanes
4114A07	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM6: PFPE (1%)+PFS2 SW3: DMF
4114A08	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM6: PFPE (3%)+PFS2 SW3: DMF
4114A09	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM6: PFPE (5%)+PFS2 SW3: DMF
4114A10	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM6: PFPE (10%)+PFS2 SW3: DMF
4114A11	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM6: PFPE (1%)+PFS2 SW3: DMF
4114A12	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM6: PFPE (3%)+PFS2 SW3: DMF
4114A13	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM6: PFPE (5%)+PFS2 SW3: DMF
4114A14	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM6: PFPE (10%)+PFS2 SW3: DMF
4114A15	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM6: PFPE (1%)+PFS2 SW3: DMF
4114A16	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM6: PFPE (3%)+PFS2 SW3: DMF
4114A17	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM6: PFPE (5%)+PFS2 SW3: DMF
4114A18	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM6: PFPE (10%)+PFS2 SW3: DMF
4114A19	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM6: PFPE (1%)+PFS2 SW3: DMF
4114A20	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM6: PFPE (3%)+PFS2 SW3: DMF
4114A21	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM6: PFPE (5%)+PFS2 SW3: DMF

4114A22	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM6: PFPE (10%)+PFS2 SW3: DMF
4114A24	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM18: PFPE (1%)+PFS2 SW3: DMF
4114A25	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM18: PFPE (3%)+PFS2 SW3: DMF
4114A26	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM18: PFPE (5%)+PFS2 SW3: DMF
4114A27	Al, PFPE	MoO_3 (dense)	Ab (Sb_2S_3)	BM18: PFPE (10%)+PFS2 SW3: DMF
4114A28	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM18: PFPE (1%)+PFS2 SW3: DMF
4114A29	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM18: PFPE (3%)+PFS2 SW3: DMF
4114A30	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM18: PFPE (5%)+PFS2 SW3: DMF
4114A31	Al, PFPE	MoO_3 (undense)	Ab (Sb_2S_3)	BM18: PFPE (10%)+PFS2 SW3: DMF
4114A32	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM18: PFPE (1%)+PFS2 SW3: DMF
4114A33	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM18: PFPE (3%)+PFS2 SW3: DMF
4114A34	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM18: PFPE (5%)+PFS2 SW3: DMF
4114A35	Al, PFPE	Bi_2O_3 (<1μm)	Ab (Sb_2S_3)	BM18: PFPE (10%)+PFS2 SW3: DMF
4114A36	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM18: PFPE (1%)+PFS2 SW3: DMF
4114A37	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM18: PFPE (3%)+PFS2 SW3: DMF
4114A38	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM18: PFPE (5%)+PFS2 SW3: DMF
4114A39	Al, PFPE	Bi_2O_3 (70μm agg)	Ab (Sb_2S_3)	BM18: PFPE (10%)+PFS2 SW3: DMF

Baseline MIC Screening

Initial batches of MIC using 80 nm aluminum and Bi_2O_3 or MoO_3 were fabricated using EMPI's MIC fabrication procedure. The MIC was then loaded into primers and tested using the ball drop tester. This resulted in the first non-factory primer to fire in the ball drop tester, but the success was minimal. Only about 10% of the primers would fire from the 20 inch drop height with the 4 oz. ball.

After discussions with the sponsor (ARDEC) and a subject matter expert (Chris Csernica), it was proposed that flaws existed in EMPI's primer loading procedure. Application specific modifications should be made to the EMPI's MIC fabrication process. The key changes to the processes are as follows:

- Fabrication
    - A binder (Viton) was incorporated
    - Less solvent was used, creating a paste like consistency rather than a slurry
    - No abrasive was used
- Loading
    - The composition was loaded into the primer cups while still wet and dried in a vacuum oven
    - No foil or paper was used
    - A convex shaped die punch was used in conjunction with an arbor press to consolidate the dried powder
    - The anvil was not seated completely flush with the rim of the primer cup

As a result of incorporating these changes, the sensitivity of the MIC primers drastically increased from a 10% fire rate at 20 inches to an impact sensitivity of between 11 and 12 inches on the ball drop tester using the 4 oz. ball. EMPI has no data with which to provide a comparison for these results, however, the improvements in sensitivity appear satisfactory. As a result, testing will move forward with developing a low-cost "green" M42 replacement primer.

Group B Formulations

The Group B Matrix of primer formulations is shown in Figure 12. Group B is designed to isolate and test a few fundamental parameters. The first series of tests, namely Group B alpha, was designed to test all available oxidizers to determine several "best performers," while using the 80 nm aluminum as the fuel since it has resulted in successful primer ignitions during the baseline MIC testing. Once three to four metal oxides have been selected based on the highest sensitivities, the 80 nm aluminum will be replaced with the low-cost 2 μm aluminum flake, and the binder component of the mixture will become the isolated component. A binder was discovered to be essential to reduce the impact sensitivity of loaded primers, and up to this point, only Viton has been tested. Therefore, Group B beta is designed to test Viton, gum arabic, and sodium silicate.

Group B Alpha

Fuel: 80 nm Aluminum

Binder: 1% Viton (wet precipitate onto oxidizer particles)

Oxidizer:

- *4114B01* – Un-densified MoO_3 (virgin)
- *4114B02* – Un-densified MoO_3 (ball milled)
- *4114B03* – 1-5µm CuO (virgin)
- *4114B04* – 1-5µm CuO (ball milled)
- *4114B05* – 1-5µm Fe_2O_3 (virgin)
- *4114B06* – 1-5µm Fe_2O_3 (ball milled)
- *4114B07* – Sub-micron Bi_2O_3
- *4114B08* – 20-40nm Fe_2O_3
- *4114B09* – 3nm Fe_2O_3
- *4114B10* – 30-50nm CuO

Group B Beta

Fuel: 2µm Aluminum flake

Binder: 1% Viton (wet precipitation onto oxidizer particles)

Oxidizer:

- *4114B11-4114BXX* – any performers from "alpha" under sensitivity threshold

Fuel: 2µm Aluminum flake

Binder: 1% Gum Arabic (H_2O solution, create "paste")

Oxidizer:

- *4114BXX-4114BXX* – any performers from "alpha" under sensitivity threshold

Fuel: 2µm Aluminum flake

Binder: 1% Sodium Silicate (H_2O solution, create "paste")

Oxidizer:

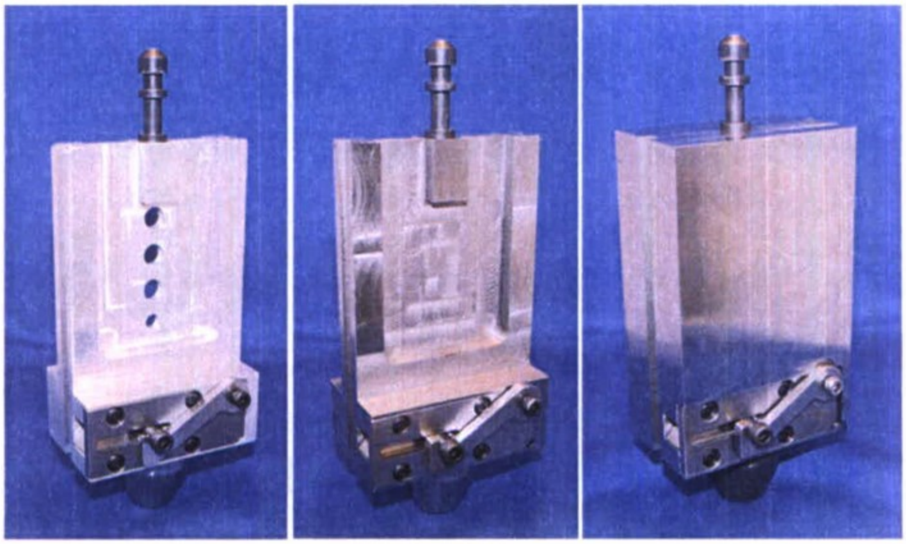
- *4114BXX-4114BXX* – any performers from "alpha" under sensitivity threshold

Figure 12 Group B Formulations

At this point in the program, EMPI was running low on empty primer cups and anvils with approximately 80 full assemblies remaining. It was decided to test the Group B alpha formulations in loose powder form in the BAM impact sensitivity tester in order to preserve primer assemblies and speed up the initial screening process.

Impact Sensitivity Testing

The BAM Impact sensitivity tester was able to test impact sensitivities in the range of 0 – 5J using the 1 kilogram drop mass. Initially, the two baseline MICs (80 nm aluminum/MoO_3 and 80 nm aluminum/Bi_2O_3) were used for testing. Neither of these materials reacted when the impact drop weight was dropped from its maximum height. In order to allow for a wider range of impact energies, a 2 kg and 5kg drop mass were designed and fabricated. The new drop masses, shown in Figure 13Figure 13, allowed for impact energies of up to 25 J to be delivered to the sample.



1 kg drop mass
Impact Energy: 0 - 5.2 J

2 kg drop mass
Impact Energy: 0 – 10.4 J

5 kg drop mass
Impact Energy: 0 – 26 J

Figure 13 BAM Impact drop masses

The baseline MIC powders were still too insensitive in the BAM tester to ignite with the 5 kg mass dropped from the maximum height. Two paths were taken to explore this unexpected result. Dr. Emily Hunt et al. from West Texas A&M University had previously published impact sensitivity data for nano-thermite powders comprised of aluminum and MoO_3 which fell well within EMPI's testing capabilities (~1.5J). Dr. Hunt was contacted and agreed to test EMPI's baseline MIC powders in WTAMU's type-12 impact sensitivity tester apparatus in order to determine if the material itself is insensitive. The results indicate that EMPI's baseline MIC materials have an impact sensitivity of approximately 0.5J, as shown in Table 6.

Table 6 Type-12 impact sensitivity tester data

Height (cm)	Run	Result (1 = +) (0 = -)	
1.6	1	0	-
1.6	2	0	-
3.2	1	0	-
3.2	2	0	-
3.2	3	0	-
3.2	4	0	-
3.2	5	0	-
4.5	1	0	-
4.5	2	1	+
4.5	3	0	-
4.5	4	1	+
4.5	5	1	+
4.5	6	1	+
4.5	7	1	+

Average Result For Height			
Height	Result	(+,-)	P. E. (J)
4.5	1	+	0.44
3.2	0	-	0.31
1.6	0	-	0.16

Al + MoO3 - 80 nm	
Drop Mass:	1.0 kg
Intermediate Drop Mass:	1.5kg

Emily Hunt et al., West Texas A&M University

As a result of this data, it was determined that EMPI's BAM impact tester is possibly flawed. Two well-known materials, HMX and picric acid, with known impact sensitivities were tested and the results were compared with published data. HMX was tested first, and EMPI ascertained an impact sensitivity of approximately 15 J, which is about twice high as the published 7.4 J. However, the HMX used could not be confirmed to be a high level of purity. As a result, lab grade picric acid was tested and EMPI's numbers agreed with the published data indicating an impact sensitivity of 20 J.

At this point, it is yet to be determined why thermitic primer composition materials cannot be ignited in the BAM impact tester with impact energies of 25 J, and can be in the type-12 apparatus at only 0.5 J. However, from this endeavor, it was apparent that loose powder impact sensitivities do not directly correlate to the sensitivities of a loaded primer cup assembly. As result, it was decided to divide the remaining primer cups (80) into 4 groups of 20 and form an abbreviated Group B matrix in order to continue testing.

Abbreviated Group B Screening

The four compositions fabricated and tested with the remaining primer cup assemblies were as follows:

- 2 μm Al flake/MoO_3 (20nm thick flakes), 1% Viton
- 2 μm Al flake/Bi_2O_3 (sub-micron), 1% Viton
- 2 μm Al flake/Fe_2O_3 (3 nm), 1% Viton
- 2 μm Al flake/CuO (30-50 nm), 1% Viton

Of the 80 primers tested, none fired in the ball drop tester apparatus when the maximum ball mass and drop height were used indicating the 2 μm aluminum flake may not be sensitive enough for a percussion primer assembly.

BAM Impact Tester Calibration

Further steps were taken to calibrate the BAM impact sensitivity tester. The first issue addressed was the leveling of the apparatus and making sure the drop hammer mass and the anvil assembly were normal to each other. The concrete base was rebuilt to ensure maximum stability, and a 1 inch layer of smooth concrete was poured on top of the base and carefully leveled. Once the concrete layer was set and level, the impact tester was re-assembled using carefully placed steel shim stock to ensure that each component was properly aligned.

Once we were confident in the setup of the apparatus, a full Bruceton analysis (40 samples) was conducted with high purity PETN. The results of this analysis are shown in Table 7. This analysis was performed with the 2 kg drop mass; therefore, the mean height of 12.257 inches correlates to an impact sensitivity of 6.1 J. No published data for PETN could be found specifically for the BAM type device, however, 6.1 J is in the same "ballpark" as several other common impact testing devices.

Table 7 Bruceton Analysis for PETN

EMPI - Bruceton Test Analysis	
7/15/2010 18:01	
Test Title: PETN	
Increment	0.75 in
Total Tested	40 in
Estimate of Mean	12.257 in
Estimate of Sigma	0.836 in
Mean +/- 5 Sigma	16.438 : 8.075 in

General Observations and Conclusions

Although the end goal of a low-cost, green percussion primer was not achieved, several important observations were made about using thermitic materials for percussion primer compositions:

- Bi_2O_3 is the best oxidizer performer of those tested
- A binder is essential to increasing sensitivity
- (1% Viton was best performer of those tested)
- Primer material must be consolidated in the cup to 10 – 20 KSI
- An arbor press and load cell were used
- Ball-milling 2 μm Al flake does not increase its impact sensitivity
- Coating 2 μm Al flake with PFPE decreases its impact sensitivity
- Drop hammer impact sensitivity is not a direct correlation to primer function sensitivity

Appendix A: BET Results for Ball Milled Aluminum

NOVACENTRIX™
NCC Nano LLC dba Novacentrix
Phone: 512.491.9500 · Fax: 512.491.0002 · www.novacentrix.com
200-B Parker Dr · Suite 580 · Austin, Texas 78728

Material Testing Results

Sample Name	Indian 2 micron Al, Ball Mill 0 hour
Customer Name	EMPI
Novacentrix Sample Number	1000-1
Sample Submission Date	2/18/2010
Report Date	3/3/2010
Specific Surface Area (m^2/gm) measured by BET Method, single point	12.0
Powder Constituent Density (kg/m^3) Aluminum handbook value	2700
Calculated Equivalent Sphere Diameter (nm)	186
Signature	[signature]
Date	3/3/10

NOVACENTRIX™
NCC Nano LLC dba Novacentrix
Phone: 512.491.9500 · Fax: 512.491.0002 · www.novacentrix.com
200-B Parker Dr · Suite 580 · Austin, Texas 78728

Material Testing Results

Sample Name	Indian 2 micron Al, Ball Mill 12 hour
Customer Name	EMPI
Novacentrix Sample Number	1000-2
Sample Submission Date	2/18/2010
Report Date	3/3/2010
Specific Surface Area (m^2/gm) measured by BET Method, single point	13.1
Powder Constituent Density (kg/m^3) Aluminum handbook value	2700
Calculated Equivalent Sphere Diameter (nm)	170
Signature	[signature]
Date	3/3/10

NCC Nano LLC dba Novacentrix
Phone: 512.491.9500 · Fax: 512.491.0002 · www.novacentrix.com
200-B Parker Dr · Suite 580 · Austin, Texas 78728

Material Testing Results

Sample Name	Indian 2 micron Al, Ball Mill 24 hour
Customer Name	EMPI
Novacentrix Sample Number	1000-3
Sample Submission Date	2/18/2010
Report Date	3/3/2010
Specific Surface Area (m^2/gm) measured by BET Method, single point	11.4
Powder Constituent Density (kg/m^3) Aluminum handbook value	2700
Calculated Equivalent Sphere Diameter (nm)	196
Signature	
Date	3/3/10

NCC Nano LLC dba Novacentrix
Phone: 512.491.9500 · Fax: 512.491.0002 · www.novacentrix.com
200-B Parker Dr · Suite 580 · Austin, Texas 78728

Material Testing Results

Sample Name	Indian 2 micron Al, Ball Mill 48 hour
Customer Name	EMPI
Novacentrix Sample Number	1000-4
Sample Submission Date	2/18/2010
Report Date	3/3/2010
Specific Surface Area (m^2/gm) measured by BET Method, single point	6.9
Powder Constituent Density (kg/m^3) Aluminum handbook value	2700
Calculated Equivalent Sphere Diameter (nm)	321

Signature

Date 3/3/10